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"Thin Films from Solvated Metal Atoms and Metal-Metal Bonded Compounds"

by

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ABSTRACT

Metals such as Pd, Pt, Cu, Ag, Ga, In, Ge, Sn, and Pb are evaporated under vacuum and the vapors (atoms) cocondensed at 77°K with excess organic solvents. In this way solvated metal atoms are produced.. Upon warmup to room temperature metal atom agglomeration occurs in certain solvents to yield stable colloidal particles in solution. In many cases these are the first examples of non-aqueous colloids of these metals, and they are very novel in that they are free of contaminating reducing agents, halide ions, etc., and they are living colloids--by removal of solvent metallic films can be grown on various substrates under very mild conditions. Characterizing these colloidal particles and the films therefrom is an important part of this project.

A second area is the proposed synthesis of new metal-metal bonded compounds, eg. $R_2Al-AlR_2$, as possible new Chemical Vapor Deposition materials for thin film production. Unusual synthetic approaches, some involving metal vapors, are underway. Compounds containing Al, Ga, In, and As are contemplated. The advantage of such material, on the microscopic level, is that two metal atoms could be deposited at a time on a hot substrate target, thereby generating films of novel structure/stoichiometry (when mixed metals are being codeposited).

A. Brief Description of Results

Our colloid and surface work continued and we have reported on Au, Pd, and In colloidal dispersions in organic solvents. Films of indium metal and indium oxide were prepared and studied. We also found that stable Au and Pd colloids can be prepared in liquid styrene, and this purple solution can be controllably polymerized to metal doped polystyrene. This is the first preparation of stable metal colloids such as these in a useful monomer medium. Unusual stabilization mechanisms for these colloidal particles are of interest:

(1) the particles appear to scavenge electrons to become negatively charged, and (2) strong solvation processes must be important. Electrophoresis studies, electron microscopy, electrolytic additions, plasmon absorption spectroscopy, and conductivity studies have been valuable in characterization of particles and films.

A second major emphasis this year has been the attempted synthesis of Al-Al, Al-As, Ga-Ga, and Ga-As bonded organometallic compounds. We have met with limited success. However, we have further elucidated the chemistry of Al and Ga atoms, and As_2 dimer. We have discovered a facile synthesis of $R_3Ga_2X_3$ which may be an important discovery since it would allow a better route to R_3Ga compounds for CVD processes.

B. Recent Findings (July 1987 to July 1988)

The dispersion of metal vapor into fluorocarbon solvents has been of interest in recent months. Metal atom clustering in cold fluorocarbons do not stabilize colloidal suspensions at room temperature, and metal powder precipitates. However, a very interesting phenomenon is that these fluorocarbon derived metal powder are "soluble" in organic solvents. A good example is gold powder derived from perfluoro-tri-n-butylamine. Upon extraction (or treatment of the filter cake) with acetone, red colloidal suspensions are obtained. The gold particles "dissolved" in this way are smaller than those obtained directly from metal atoms dispersed in acetone.

For example, fluorocarbon derived particles are 10-40Å, while acetone derived are 50-90Å. Furthermore, the particles retain fluorocarbon; that is, according to X-ray fluorescence they are true gold but their surfaces appear to be fluorocarbon coated, thus their strange molecular behavior (ability to be dissolved and small size).

We have also discovered that monomers such as styrene and methylmethacrylate can stabilize colloidal dispersions of Cu, Ag, Au, and Pd. Polymerization of these colored solutions yields homogeneous metal doped polymers. This procedure works extremely well and allows the synthesis of various loadings of metal doped polymers.

C. A Listing of Technical Reports Submitted

1. S. T. Lin, M. T. Franklin, and K. J. Klabunde, "Non-Aqueous Colloidal Gold. Clustering of Metal Atoms in Organic Media, 12," Langmuir, 2, 259 (1986).

2. K. J. Klabunde, editor, "Thin Films From Free Atoms and Particles,"' Academic Press, Orlando (1985).

3. K. J. Klabunde, "Introduction to Free Atoms and Particles," Chapter in 2 above.

4. G. Nieman and K. J. Klabunde, "Clustering of Free Atoms and Particles: Polymerization and Film Growth," Chapter in 2 above.

5. M. Franklin and K. J. Klabunde, "Living Colloidal Metal Particles from Solvated Metal Atoms: Clustering of Metal Atoms in Organic Media", Sym. High Energy Processes in Organomet. Chem., K. Suslick, editor, ACS Sym. No. 333, pg. 246 (1987).

6. G. Cardenas-Trivino, K. J. Klabunde, and B. Dale, "Living Colloidal Palladium in Non-Aqueous Solvents. Formation, Stability and Film Forming Properties. Clustering of Metal Atoms in Organic Media. 14", Langmuir, 3, 986 (1987).

7. G. Cardenas-Trivino, K. J. Klabunde, and B. Dale, "Thin Metallic Films from Solvated Metal Atoms", Proceedings of SPIE, Vol. 821, 206 (1987).

8. K. Starowieyski and K. J. Klabunde, "Reactions of Vapors of Some Metals and Metal Oxides with Organometallics of Main Group Elements", Submitted to App. Organomet. Chem.

9. G. Cardenas-Trivino and K. J. Klabunde, "Characterization of Metallic Thin Films Prepared by Chemical Liquid Deposition (CLD): Living Colloidal Metal Particles in Non-Aqueous Solvents", Journal of the Chemical Society of Chile, in press.

10. G. Cardenas-Trivino and K. J. Klabunde, "Thermal Degradation Studies and Scanning Electron Microscopy Studies of Pd Thin Films", XVIII Latin-American Chemical Congress, Santiago, Chile, January 1988.

11. G. Cardenas-Trivino and K. J. Klabunde, "Synthesis, Stability, and Structure of Metal Colloidal Dispersions in Non-Aqueous Solvents", XVIII Latin-American Chemical Congress, Santiago, Chile, January 1988.

12. J. Habdas and K. J. Klabunde, "Preparation of Colloidal Au, Ag, Pd, and Cu in Styrene, Polystyrene, Methylacrylate and Polymethylacrylate", to be submitted to _Macromolecules_.

13. E. Zuckerman and K. J. Klabunde, "Metal Clusters or Metal Colloids?" Clustering of Metal Atoms in Fluorocarbon Media." Submitted to _Chemistry of Materials_.

D. Importance of Past ONR Supported Work

The major contributions have been the discovery that colloidal metal particles can be prepared by agglomeration of solvated metal atoms, exploring part of the scope of this process, learning about particle stabilization mechanisms, and demonstrating that metal films can be prepared from these colloidal solutions. This work has opened up a new dimension in colloid chemistry and potentially in thin film production.

The attached reprints (two of thirteen technical reports)[1,2] discuss the history of colloidal metal particles and emphasize the novelty of our discovery. As a partial reiteration of the reasons such colloidal solutions are unique: (1) they are non-aqueous, (2) no metal salts reducing process is used so no biproducts are present as impurities, (3) the metal particles are "living"' in the sense that simply by solvent removal particle growth occurs until films result, (4) films can be deposited on irregularly shaped objects, (5) the method allows particle deposition inn polymer matrices, and (6) particle size can be controlled by metal: solvent ratios, solvent choice, and warm-up procedures.

Industrial interest in these colloidal solutions as film precursors has been extremely gratifying. Shortly after announcing our findings[1,2] (after filing for patent protection),[3] a series of events took place: a major company has expressed their interest to license the patent and is paying the patent fees (the P. I. is a consultant for this company); the findings were summarized in three research and development magazines;[4] the P. I. was invited to speak at an international meeting of optical engineers (SPIE meeting in San Diego); reprint requests have been numerous; phone calls and letters from numerous industrial firms requesting more information and samples were received (the names of these forms can be provided on a confidential basis).

The firms interested in this technology invariably wanted to know if we could produce films on irregularly shaped objects such as metal parts, screens, and fabrics. Often such substrates cannot be coated by conventional vacuum evaporation/deposition methods. Another general theme was the need to deposit metal particles on or in composite materials or organic polymers. These and other interactions convince us that the work we are doing is certain to be useful to many high technology companies.

(These same scientists have expressed considerable general interest in a book the P. I. edited on "Thin Films from Free Atoms" and Particles.")[5]

E. Equipment Acquired

During the ONR supported period some important pieces of equipment have been built or purchased and brought into operation.

(1) Computerized Mossbauer Spectrometer with low temperature (as low as $4°K$)
(2) Electrophoresis equipment
(3) Thin film spray apparatus
(4) Conductivity measuring devices
(5) Additional metal vapor deposition equipment

F. People Who Have Participated in the Project

G. Cardenas-Trivino (Postdoc)
Ellis Zuckerman (Postdoc)
J. Habdas (Postdoc)
M. Franklin (Grad. Student)
S. T. Lin (Postdoc)
S. Antrim (Undergrad.)
K. Starowieyski (Visiting Prof.)
G. Nieman (Visiting Prof.)
B. Dale (Collaborating Physicist)
B. J. Tan (Grad. Student)

References

(1) G. Cardenas-Trivino, K. J. Klabunde, and B. Dale, Langmuir, 3, 986 (1987).
(2) M. Franklin and K. J. Klabunde, Symposium on High Energy Processes in Organomet. Chem., K. Suslick, editor, ACS Sym. No. 333, pg. 246 (1987).
(3) Patent Application, K. J. Klabunde, "Stable Colloidal Metal Dispersions and Conductive Films Therefrom," Serial No. 853,0277 filed April 17, 1986. A continuation in part "Substrates Coated with Solvated Clusters of Metal Particles," CIP of Serial No.. 853,027 filed March 2, 1987.
(4) B. J. Spalding, "High Hopes for Metal Vapor Chemistry," Chemical Week, July 16, pg. 34-35 (1986); Chemical and Eng. News, Sept. 22, pg. 41 (1986) Advanced Coatings and Surface Technology (a monthly intelligence service from Technical Insight, Vol. 1, No. 1. pg. 2 January (1988).
(5) K. J. Klabunde, editor, "Thin Films from Free Atoms and Particles," Academic Press, Orlando (1985).

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High-Energy Processes in Organometallic Chemistry

Kenneth S. Suslick, EDITOR
University of Illinois at Urbana–Champaign

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September 7-12, 1986

Chapter 15

Living Colloidal Metal Particles from Solvated Metal Atoms: Clustering of Metal Atoms in Organic Media

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A review of preparative methods for metal sols (colloidal metal particles) suspended in solution is given. The problems involved with the preparation and stabilization of non-aqueous metal colloidal particles are noted. A new method is described for preparing non-aqueous metal sols based on the clustering of solvated metal atoms (from metal vaporization) in cold organic solvents. Gold-acetone colloidal solutions are discussed in detail, especially their preparation, control of particle size (2-9 nm), electrophoresis measurements, electron microscopy, GC-MS, resistivity, and related studies. Particle stabilization involves both electrostatic and steric mechanisms and these are discussed in comparison with aqueous systems.

Graham coined the term "colloid" to describe suspensions of small particles in a liquid.(1) Such particles are generally considered to be from 1 to 5000 nm in diameter and are not easily precipitated, filtered, or observed by ordinary optical microscopes. The topic of this paper is metallic colloidal particles, often called metal sols, with special emphasis on non-aqueous media. Some history of gold sols is appropriate.

Gold has held the attention of mankind for thousands of years. Attempts to make the "perfect metal" (gold) from imperfect metals was the realm of alchemists, and over the centuries great medicinal powers were ascribed to gold. And as early as 300 A.D. there are references to the consumption of gold fluid to prolong life.(2) It is doubtful that this was a colloidal solution of gold since aqua regia(3) was unknown to early Chinese alchemists, and more likely amalgams of Hg-Au were actually consumed. Centuries later more recipes for *aurum potabile* (drinkable gold) appeared which were aqueous gold colloid solutions prepared by dissolving gold in aqua regia followed by treatment (chemical reduction of $AuCl_4$ or $HAuCl_4$ to Au metal particles) with ethereal oils. These solutions were usually then treated with chalk to neutralize the acid before being

consumed. Fabulous curative powers were attributed to these solutions, especially toward heart disease. And in 1618 Antoni published *Panacea Aurea: Auro Potabile*(4) which centered on the treatment of venereal diseases, dysentery, epilepsy, tumors and more with drinkable gold. Additional similar books appeared,(5) and Helcher pointed out that the addition of boiled starch noticeably increased the stability of the preparation. In 1802 Richter(6) mentioned that the shades of color in purple gold solutions and ruby glass were due to the presence of finely divided gold. He correlated the colors with particle size in a qualitative way.(4) And Fulhame(7) noted in 1794 that she could dye silk cloth various shades of purple with colloidal gold solutions. Cassius(8) and Glauber(9) were also involved in using colloidal gold as a coloring agent.

Faraday published the first scientific investigations of gold sols.(10) He usually reduced aqueous solutions of $AuCl_3$ with phosphorous. However, he also experimented with sparking gold wires. He concluded that gold was present in the solutions as elemental gold, and that color depended on particle size. He also discovered flocculation by addition of an electrolyte NaCl. Other workers also used sparking of metals under water to produce sols of Pb, Sn, Au, Pt, Bi, Sb, As, Tl, Ag, and Hg.(11-12) As the years passed aqueous colloidal gold was studied extensively. The classic work of Svedberg,(13) Zsigmondy,(14) Kohlschutter,(15) and Turkevich(16) must be noted. Zsigmondy,(14) using a slit microscope, was able to study the "seeding" phenomenon and found that gold particles already present preferentially grew as more gold salt was reduced. This and related work(17-18) improved our understanding of particle nucleation and growth.

Non-Aqueous Colloidal Metal Solutions. It has been difficult to prepare colloidal gold in non-aqueous media due to limitations in preparative methods (low salt solubilities, solvent reactivity, etc.), and the fact that the low dielectric constant of organic solvents has hindered stabilization of the particles. In aqueous solution the gold particles are stabilized by adsorption of innocent ions, such as chloride, and thus stabilized toward flocculation by the formation of a charged double layer, which is dependent on a solvent of high dielectric constant. Thus, it seemed that such electronic stabilization would be poor in organic media.

In spite of these difficulties, some limited successes have been reported. Svedberg(13) struck an electric arc in a glass tube under organic liquids. Gas flow through the tube carried some of the metal particles into the solution (liquid methane or isobutanol were used). Mayer used a similar method using very high voltage with organic-water mixtures.(19) More recently, Kimura and Bandow reported a similar method where metals were evaporated and swept into a cold trap containing ethanol, with some success.(20)

Additional successes have been reported: Svedberg(21) used an alternating current discharge to disperse small pieces of metal; Natanson(22) obtained colloidal copper in an acetone/toluene/1-pentanol mixture by reducing $CuCl_2$ with zinc powder; Janek and Schmidt(23) added a gold/citrate aqueous sol to an alcohol/toluene mixture followed by heating and cooling and found that some gold

colloidal particles remained in the alcohol rich layer. Marinescu(24) reported that sonication of alkali metals at their mp in kerosene yielded pyrophoric colloids; Yamakita(25) used fats, organic acids, alcohols, and other organics as reducing agents for Au_2O_3 and obtained success especially with fats and fatty acids; and Ledwith(26) was able to reduce $AuCl_3$ in water with diazoethane followed by mixing with organics which gave some gold particles in the organic phase.

Protective Colloids. Another approach in preparing and stabilizing metal colloids is by adsorption of macromolecules on their surfaces. A wide variety of materials have been used including gummy gelatinous liquids,(10) albumin,(27) Icelandic moss,(28) latex,(22) polyvinylpyrrolidone,(29) antibodies,(30) carbowax 20M,(31) polyvinylpyridine,(31) and various polymer-water/oil-water mixtures.(32) These studies clearly indicate that "steric stabilization" of metal colloids is also important (along with electronic stabilization).(33)
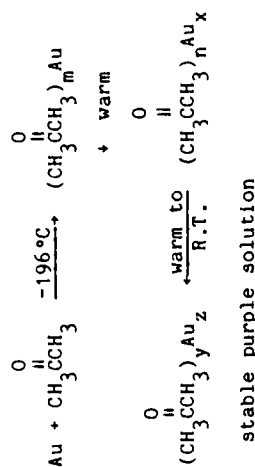
Results and Discussion

More direct and successful methods for the preparation of non-aqueous metal sols are desirable. Especially valuable would be a method that avoids the metal salt reduction step (and thus avoids contamination by other reagents), avoids electrical discharge methods which decompose organic solvents, and avoids macromolecule stabilization. Such a method would provide pure, non-aqueous metal colloids and should make efficient use of precious metals employed. Such colloids would also be valuable technologically in many ways. They would also be valuable to study so that more could be learned about particle stabilization mechanisms in non-aqueous media, of which little is known at the present time.

We have reported numerous studies of the clustering of metal atoms in non-aqueous (organic) media.(34) And very recently our preliminary report of stable non-aqueous gold sols appeared.(35) The approach has been to disperse metal atoms in excess cold organic solvent thus forming solvated metal atoms. Upon warming atoms clustering takes place moderated by solvation. Particle (cluster) growth is eventually inhibited and stopped by strongly bound solvent molecules. As mentioned above, there is some precedent for this approach found in earlier work on the preparation of active metal slurries,(36) dispersed catalysts,(37) and metal atom clustering in polymer oils.(38) However, our initial report(35) was the first describing the preparation of stable metal sols by the solvated metal atom method.

The experimental apparatus used consisted of a stationary metal atom-vapor reactor which has been detailed in the literature earlier.(39) Metal was evaporated (~0.1 to 0.5 g) and codeposited at -196°C with excess organic solvent vapor (~ 40-150 mL). The frozen matrix was allowed to warm under controlled conditions, and upon melting stirring was commenced. After warming to room temperature stable colloidal solutions were obtained and syphoned out under N_2.

A variety of metals have now been investigated in our laboratory including Fe, Co, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, In, Ge, Sn, and Pb. Solvents employed have been acetone, ethanol, THF, diethylether, dimethylsulfoxide, dimethylformamide, pyridine, triethylamine, isopropanol, isopropanol-acetone, toluene, pentane, and water. Acetone-Au will be discussed in detail herein, along with Ag.

$$Au + CH_3\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}CH_3 \xrightarrow{\ -196\,°C\ } (CH_3\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}CH_3)_m Au$$

$$\downarrow warm$$

$$(CH_3\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}CH_3)_y Au_z \xrightleftharpoons[\ ]{\ warm\ to\ R.T.\ } (CH_3\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}CH_3)_n Au_x$$

stable purple solution

Formation and Stabilization of Colloidal Solutions

Concentration Effects. In order to determine if particle size and distribution could be controlled, we prepared a series of colloidal Au-acetone solutions of varying concentrations. A drop of each solution was placed on a carbon coated copper grid, and after acetone evaporation analyzed by transmission electron microscopy (TEM). Lower concentrations of Au in acetone (0.002 M) yielded smaller particles, and at very low concentrations quite good selectivity to a certain size was possible (1-3 nm). Higher concentrations of gold yielded larger particles with a broader distribution (4-7 nm), and still higher concentration (0.04 M) gave particles 6-9 nm with some as large as 20 nm (see Figures 1-3). Figure 4, a TEM micrograph of Au particles from acetone, shows that the particles appear spherical or oblong in shape and do not show crystalline faces or certain geometrical structures. The non-crystalline nature of these particles is not surprising since, as shown later, they do contain substantial portions of organic material. Their tendency to chain together might also be explained by the presence of organic residues.

The control of particle size by concentration indicates that particle growth is a kinetic phenomenon. It is unlikely that particle growth is reversible; once a Au-Au bond is formed it would not break under these experimental conditions. In a dilute solution of atoms, the frequency of encounters would be lower. As the gold atom-solvent matrix warms, the atoms and subsequent metal particles become mobile. It is the number of encounters that occur before particle stabilization that is important. If metal concentration is high the frequency of encounters is higher and the particles become bigger.

Interestingly, Tunekevich and coworkers(16,40) report the reverse effect for gold particle growth in aqueous media. Low concentrations of $HAuCl_3$ were reduced in solution and comparatively
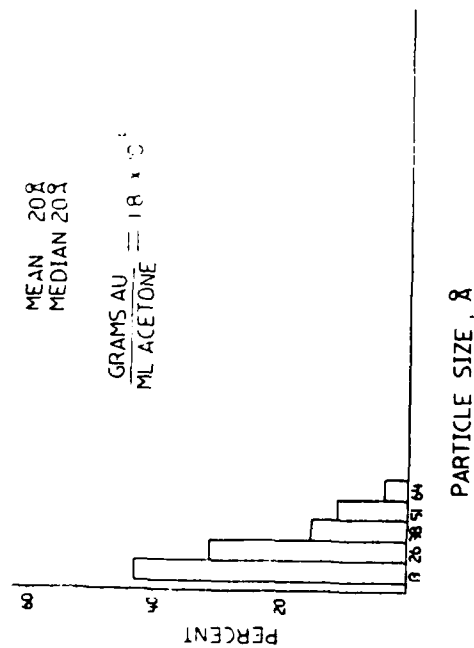
MEAN   80 Å
MEDIAN 60 Å

$$\frac{GRAMS\ AU}{ML\ ACETONE} = 91 \times 10^{-4}$$

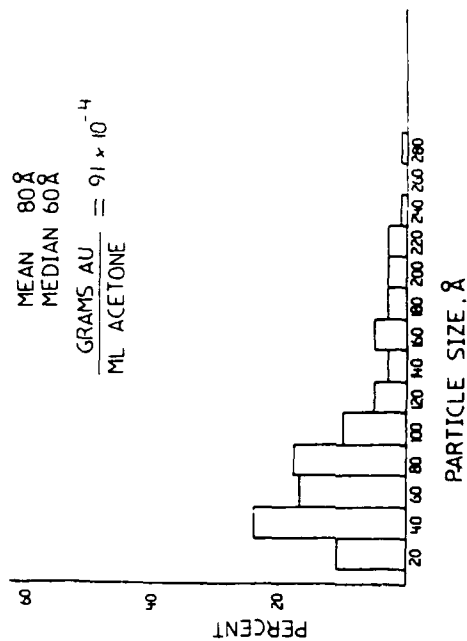PERCENT

PARTICLE SIZE, Å

Figure 3. Particle Size Distribution (High Au:Acetone Ratio)
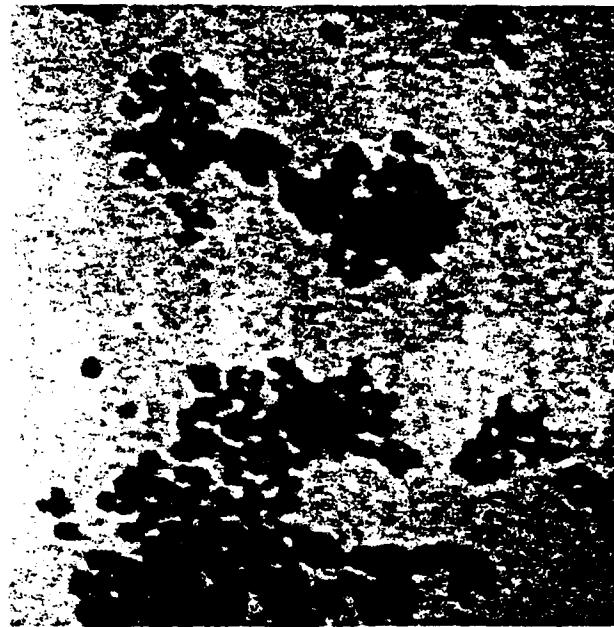
Figure 4. TEM Micrograph of Au Particles From Acetone (Individual Particles about 8 nm that chain together)

MEAN   20 Å
MEDIAN 20 Å

$$\frac{GRAMS\ AU}{ML\ ACETONE} = 18 \times 10^{-4}$$

PERCENT

PARTICLE SIZE, Å

Figure 1. Particle Size Distribution (Low Au:Acetone Ratio)

MEAN   57 Å
MEDIAN 50 Å

$$\frac{GRAMS\ AU}{ML\ ACETONE} = 2 \times 10^{-4}$$

PERCENT

PARTICLE SIZE, Å

Figure 2. Particle Size Distribution (Medium Au:Acetone Ratio)

large gold particles with a broad distribution resulted. At higher concentrations of $HAuCl_3$, the mean particle size decreased and the size distribution narrowed. Evidently a certain critical concentration of reduced auric ions was necessary in order that they would agglomerate into a stable particle. Due to the statistical nature of physical events (encounters) this required local concentration would be achieved more readily in a concentrated solution, leading therefore predominantly to rapid nucleation rather than particle growth, which is slower.

Concentration effects for Ag-acetone were also studied in our laboratory. These colloidal solutions were black as compared with purple for Au-acetone. They were also sensitive to light (see later). According to TEM the Ag particles from acetone were much larger (~ 30 nm) compared with Au (2-9 nm). The Ag particles appeared to be denser and perhaps more crystalline. They contained much less organic residue than the Au particles. Particle size for Ag was also dependent on Ag-acetone concentration in the same way as for Au, and the Ag particles were more polydisperse ranging from 20-40 nm.

Matrix Warmup:

Earlier we reported that Ni-pentane matrices upon warming from -196°C yielded tiny Ni particles that incorporated substantial organic material from fragmented pentane (34). The amount of organic material (mainly C_1 fragments) could be increased and the Ni particle sizes decreased by allowing the Ni-pentane matrix to warm slowly.

Somewhat analogous behavior has been observed with these Au-acetone matrices. The most striking finding is that slow warmup (2h from -196°C to 25°C) was necessary to achieve a stable purple colloidal solution. Rapid warmup invariably caused excessive particle growth and flocculation/precipitation of the Au particles. However, incorporation of organic residues does not appear to be the reason for this behavior since the resultant dry Au films (after acetone stripping) did not show significant or systematic changes with initial Au solvent ratio. In the case of Au-acetone and Pd-acetone(41) we suspect two reasons for this behavior: (1) solvent reordering and displacement during particle growth may be a slow process and (2) Au and Pd particles acquire negative charge, which helps stabilize their colloidal nature, and this is probably a slow process (discussed next under the electrophoresis section).

Electrophoresis. Electrophoresis, the movement of charged particles in response to an electric potential, has become very important in biochemistry and colloid chemistry. In the present study an apparatus similar to that described by Burton(42-45) was used. A U-tube with an inlet at the bottom and removable electrodes at the two upper ends was half filled with acetone. The a Au-acetone colloidal solution was carefully introduced from the bottom so that a sharp boundary was maintained between the clear acetone and the dark purple colloid solution. Next, platinum electrodes were placed in the top ends of the U-tube, and a DC potential applied. The movement of the boundary toward the positive pole was measured with time. Several Au-acetone colloids were studied, and electrophoretic velocities determined as 0.76-1.40 cm/h averaging 1.08 cm/h.

Calculation of electrophoretic mobility μ takes the potential into account:

$$\text{electrophoretic velocity} = \frac{1.08}{3600 \text{ s}} = 30 \times 10^{-5} \text{ cm/s}$$

$$\text{electrophoretic mobility} = \mu = 30 \times 10^{-5} \text{ cm s}^{-1} / 12.67 \text{ V}$$

$$\mu = 2.36 \times 10^{-5} \text{ cm/V} \cdot \text{s}$$

This value can be compared with those reported for a variety of aqueous colloidal particles, eg colloidal gold - $30\text{-}40 \times 10^{-5}$ (< 100 nm particle diameter), colloidal platinum - 20×10^{-5} (< 100 nm), colloidal lead - 12×10^{-5} (< 100 nm), and oil droplets - 32×10^{-5} (2000 nm). (43,44). The similarities of these numbers regardless of particle size suggests that the larger the particle is, the more negative charge it acquires.

The relation between electrophoretic mobility μ and the surface properties of the particle (usually modeled as an ionic double layer for aqueous systems) is a classical problem in colloid science.

The Helmholtz-Smoluchowski equation is probably the oldest solution to $\mu = \frac{\varepsilon \xi}{4\pi \eta}$.

μ = electrophoretic mobility
ξ = electrokinetic potential (zeta potential)
ε = dielectric constant of the medium
η = viscosity of the medium (Stokes)(4b)

$$\mu = \frac{\varepsilon \xi}{4\pi \eta}$$

the problem, but is known to be rather restricted. Huckel(47-48) considered electrophoretic retardation forces as well and proposed:

$$\mu = \frac{\varepsilon \xi}{6\pi \eta}$$

Henry(49) took into account the deformation of the applied D.C. field and proposed:

$$\mu = \frac{\varepsilon \xi}{6\pi \eta} f_1(\kappa a)$$

The dimentionaless κa is a measure of the ratio between the particle radius and the thickness of the ionic double layer. In the limit $\kappa a \to \infty$ (the double layer is very thin compared with particle radius $f_1(\kappa a) - 3/2$ and the result is the Helmholtz-Smoluchowski equation. In the limit $\kappa a \to 0$, $f_1(\kappa a) - 1$ and Huckel's result is obtained.

Application of any of these expressions to our Au-acetone colloid system poses some problems. First, according to these theories the charge on the particle is supposed to result from the tight adsorption of negative ions and an outer more loosely attracted layer of counterions stabilizes the similarly charged outer layers of other particles, preventing coagulation.(50) Although our Au-acetone system must contain some kinds of positively charge species to preserve electrical neutrality, the nature of this species is unknown. Also, all the equations derived have been worked out for aqueous systems.

The Huckel equation where $\kappa a \to 0$ is the one most likely to be applicable to electrophoresis in non-aqueous media:(44)

$$\mu = \frac{\varepsilon \zeta}{6\pi\eta}$$

Solving for ξ: $\quad\xi = \frac{\mu 6\pi\eta}{\varepsilon}$

Substituting the appropriate values:(41,51)

$$\xi = 768 \text{ mv}$$

This value is considerably larger than those reported earlier for aqueous metal sols:(43) colloidal gold - 58 mv, 32 mv; platinum - 44 mv, 30 mv; lead - 18 mv. However, such large values might be expected for a low dielectric medium such as acetone.

Although comparison of these values with those determined in aqueous systems is tenuous, it is clear that the Au particles do possess considerable negative charge. Where this charge comes from is puzzling. It is possible that organic free radicals formed by pyrolysis or by homolytic bond breaking on Au atoms could transfer electrons to Au particles. A number of radiolysis studies of metal colloids in water-acetone solutions indicate that organic radicals do transfer electrons, and the particles act as electron reservoirs (and can behave as catalysts for water reduction).(52,53)

$$(CH_3)_2\dot{C}OH + (Ag)_m \rightarrow (CH_3)_2C^+\text{-}OH + (Ag)_m^-$$

$$CH_3\overset{O}{\overset{||}{C}}CH_3 + H^+ + (Ag)_m^-$$
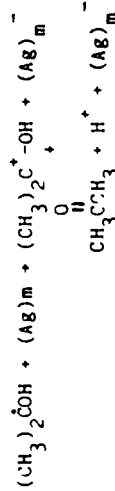
If such a process was involved in our system, the generation of H^+ in solution would be expected. We have found no evidence for this (pH measurements, conductivities).

A second possibility is that the Au particles scavenge electrons from the reaction electrodes, walls and solvent. This is the explanation we favor at the present time since we have been able to effect changes in electrophoretic mobilities by supplying electrical potential to the colloid solution as the particles form,(41) and the fact that such charging has been reported before, for example with oil droplets in water.(43)

Spectroscopic Studies:

UV-visible spectra of the Au-acetone sols showed absorptions at 706 and 572 nm, the latter being attributed to plasmon absorption.(54) We have found that the plasmon absorption was not a good indicator of true particle size (obtained by TEM) since the 572 band did not shift significantly with particle size.(35) However, in aqueous solution this band has been used successfully to roughly determine particle size.(55)

NMR studies of acetone stripped from colloidal solutions showed no reaction products.

Conductance Studies:

The conductance of several Au-acetone colloids was measured and compared to pure acetone, and NaI-acetone solutions. As expected the NaI-acetone solutions (0.00075 M up to 1.5 M) showed greatly increased conductivities (130 to >20,000 μohm s^{-1} cm^{-1}). However, the Au-acetone colloid solutions showed approximately the same conductivities (2.5 to 7.4 μohm s^{-1} cm^{-1}) as acetone itself (4.5 μohm s^{-1} cm^{-1}). We conclude that very little "electrolyte" (ion pairs) was present in the purple Au-acetone colloidal solutions.

Temperature Sensitivity. Samples of Au-acetone colloid were subjected to boiling and freezing. Upon returning to room temperature the colloids remained stable and no flocculation had occurred. These results indicate that steric stabilization(33,43) (solvation) is a very important mechanism. Charge-stabilized colloids generally flocculate when subjected to such extremes of temperature.(56)

Light Sensitivity. The initially purple-black Ag-acetone colloid solutions turned grey and the Ag precipitated as a spongy grey mass upon exposure to room light for 3-4 days. However, in the dark the colloid solutions remained stable indefinitely.

Particle Formation and Stabilization-Preliminary Conclusions:

Gold atoms dispersed in excess acetone (or other solvents) begin to cluster upon warming form -196°C. Particle (cluster) growth is moderated by two stabilizing mechanisms: (1) strong solvation which is a form of steric stabilization, and (2) electron scavenging to form negatively charged particles, which is a form of charge stabilization. Ultimate particle size is also affected by initial metal concentration and by warmup time, which suggests that the rates for these processes (stabilization vs growth) are competitive and can be controlled somewhat by time and temperature. Thus, purely kinetic phenomena appear to be involved.

Film Formation. A novel feature of these Au-organic solvent colloids is their film forming properties that can be induced simply by solvent stripping. In this sense they are "living" colloidal particles. Films formed in this way are conductive, but less so than pure metals.(41) The higher resistance of the films is due to the incorporation of substantial portions of the organic solvent, which can partially be removed by heating, and resistivity then decreases.(41)

Elemental Analyses. After solvent (acetone) stripping at room temperature (10^{-3} Torr for 1 h) Au films were scraped out and elemental analyses obtained. Variable results were obtained where Au ranged from 63-83% by weight, C from 6-17%, H form 0.8-1.1, and oxygen (by difference) from 6-17%. A heated sample yielded much lower C and H (0.62 C and < 0.01 H). Silver films showed much lower values for C and H.

Pyrolyses. A film from Au-acetone was pyrolyzed in stages up to 300°C. At intervals mass spectra were recorded, which showed the evolution of acetone (mainly) as well as other products. A similar experiment, where GC-MS was employed allowed identification of several of these minor products as CO_2, H_2O, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, C_4H_6O, and C_4H_2 (probably butadiyne). Pyrolysis of adsorbed acetone may be the source of these materials.

Similar treatment of a Ag film from acetone only evolved some CO_2.

Infrared Studies. A gold residue from acetone was mixed with KBr and compressed to a pellet. Numerous IR scans were accumulated, and the spectrum indicated the presence of adsorbed acetone (mainly).

2960 and 1750 cm^{-1}). However, weaker bands at 2580, 1635, and 570 were also observed which perhaps indicate strongly chemisorbed acetone, as Weinberg(57) has recently reported on a Ru surface. The 570 cm band is probably due to ν_{Au-C}.(58)

Resistivity. A film was prepared by dripping a colloidal Au-acetone solution on a glass plate edged with silicon rubber adhesive resin. The acetone was allowed to evaporate, and resistivity was measured by trimming the film to a rectangular shape. It was connected to electrodes on each end by vapor depositing an opaque film of copper, and resistance measured with a Digital Multimeter KEITHLEY 178 Model, with the following results: Thickness of film = 4.5 μm, resistance = 46 Ω/cm, resistivity $\rho(\Omega \cdot cm) = 1.8 \times 10^{-6}$.(51) Thus, the gold film from Au-acetone is more than 7000 times less conductive due to the incorporation of organic material.

Film Formation-Preliminary Conclusions:

Removal of solvent allows the colloidal particles to grow to a film. However, strongly adsorbed acetone, and perhaps small amounts of acetone fragments or telomers as well, remain in the film affecting its electrical properties.

Experimental Section

Preparation of a Typical Au-Acetone Colloid. The metal atom reactor has been described previously.(39,59,60) As a typical example, a W-Al$_2$O$_3$ crucible was charged with 0.50g Au metal (one piece). Acetone (300 mL, dried over K$_2$CO$_3$) was placed in a ligand inlet tube and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 1×10^{-4} Torr while the crucible was warmed to red heat. A liquid N$_2$ filled Dewar was placed around the vessel and Au (0.2g) and acetone (80g) were codeposited over a 1.0 hr period. The matrix was a dark purple color at the end of the deposition. The matrix was allowed to warm slowly under vacuum by removal of the liquid N$_2$ from the Dewar and placing the cold Dewar around the reactor.

Upon meltdown a purple solution was obtained. After addition of nitrogen the solution was allowed to warm for another 0.5 hr to room temperature. The solution was syphoned out under N$_2$ into Schlenk ware. Based on Au evaporated and acetone inlet the solution molarity could be calculated.

Electrophoresis Experiments. The electrophoresis experiments were carried out by using a glass U-tube of 11.0 cm each with a stopcock on the base to connect a perpendicular glass tube 13 cm long and 35 cm high.(43,45) Platinum electrodes were attached to the top of the U-tube and through a ground glass joint to the pole of a 12V battery. The acetone was placed in the U-tube and then the colloid solution added slowly through the lower tube. The migration rate was determined based upon the average of the displacement in each side of the U-tube. A typical experiment was carried out for a period of 3 hr. at 25°C.

GC-MS Experiments. GC-MS pyrolyses were carried out using a Porapak Q column 6-ft (flow rate 35 mL/min) attached to a Finnigan 4000 quadrupole GC-MS. The sample was placed in a stainless steel tube 10 cm long connected to a 4 way valve. One of the outlets was attached to a Porapak Q column interfaced with the M.S. The stainless steel tube containing a portion of Au colloid film was placed in a furnace connected to a Variac provided with a digital quartz pyrometer to measure the temperature. Three pyrolyses were performed at 100, 200 and 350°C with the Au-acetone film.

TEM Studies. Electron micrographs were obtained on JEOL, TEMSCAN — 100 CX11 combined electron microscope and a HITACHI HV-11B (TEM) operated at 2×10^5 magnification. The specimens for TEM were obtained by placing a drop of the colloid solution on a copper grid coated by a carbon film.

Infrared Red Studies. Infrared spectra were recorded in a Perkin Elmer PE-1330 infrared spectrometer. IR studies of the metal films using either KBr pellets or Fluorolube yielded bands at 2960(s), 2580(m), 1750(s), 1635(m), and 570(w) cm^{-1}.

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Living Colloidal Palladium in Nonaqueous Solvents. Formation, Stability, and Film-Forming Properties. Clustering of Metal Atoms in Organic Media. 14

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Palladium atoms in cold acetone, ethanol, and other organic solvents cluster to form living colloidal particles. The Pd colloids are stable for months at room temperature in acetone, and their particle sizes (about 8 nm) vary slightly according to the solvent:Pd ratio and warming procedures. The particles are stabilized by both steric stabilization (solvation) and by incorporation of negative charge. They are "living" in the sense that production of larger particles and films can be accomplished simply by solvent removal. The Pd films formed at room temperature by solvent evaporation have semiconductor properties (rather than metal-like conductivity) due to the incorporation of substantial portions of organic solvent (and small amounts of solvent fragments). Upon heat treatment the films become smoother, give up organic solvent, and decrease in resistivity. These are the first examples of nonaqueous Pd colloids and the first examples of film formation from such colloidal solutions.

Introduction and Background

Although colloidal metal particles in aqueous media are well-known,[3] preparations in nonaqueous media have been hampered by low stability of the colloids presumably due to ineffective stabilization mechanisms (low solvent dielectric constant, low viscosity, etc.) and preparative methods. However, we have recently reported a successful, new approach to the preparation of stable metal colloids in nonaqueous media based on the process of atom clustering at low temperature.[4] This process appears to be very wide in scope, and the resultant colloidal particles are free of interfering ions and impurities usually present in aqueous preparations. In addition, they are "living colloids" since particle growth to films occurs under very mild conditions and can be induced simply by solvent evaporation. In this paper we report details on nonaqueous palladium colloids.

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(3) Turkevich, J.; Stevenson, P. C.; Hillier, J. *Discuss. Faraday Soc.* 1951, *11*, 55–75.
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Palladium and Platinum Colloids. Some years ago Rampino and Nord[5] prepared Pd and Pt catalysts in which synthetic high molecular weight polymers were used as protective coatings (steric stabilization of colloidal particles).[6] Palladium–methyl methacrylate was prepared by the addition of glacial acetic acid to methyl methacrylate (MMA) followed by the addition of palladium chloride solutions. Similarly, palladium–poly(vinyl alcohol) was prepared and shown to be a very efficient hydrogenation catalyst. The palladium–poly(vinyl alcohol) and platinum–poly(vinyl alcohol) catalysts were equally active in acid, neutral, and alkaline media.
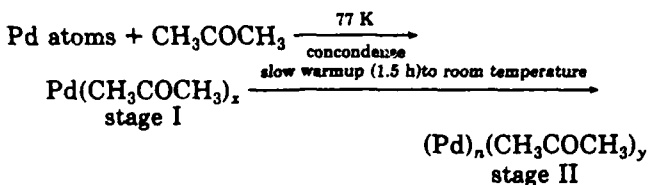
Stable aqueous Pt sols (colloidal particles) have been prepared by the citrate reduction of chloroplatinic acid.[7] It was found that the Pt particle size and the extent of reduction of the chloride salt increased with temperature. These Pt sols with particle diameters in the range 1.5–4 nm exhibited great resistance to coagulation by electrolytes such as LiCl, NaCl, KCl, CsCl, $MgCl_2$, $SrCl_2$, $CaCl_2$, $BaCl_2$, and $AlCl_3$. It was also found that H_2 treatment caused particle growth to about 5 nm.

Colloid Stabilization. There are two principle mechanisms for stabilization of metallic colloids: (1) electrostatic, colloidal particle charging due to adsorption of innocent ions in the solution[8] (such as chloride ion), and (2) steric, solvent ligation or polymer adsorption or ligation. Addition of polymers to aqueous or nonaqueous colloid solutions can have significant stabilization effects due to steric features or due to depletion stabilization (rejection of polymer molecules from the interparticle region is not favored thermodynamically due in large part to proper solvent choice).[6,9,10] Polymer stabilization is very important industrially for such products as paints, inks, and food emulsions and for oil recovery, waste treatment, etc.[6,11,12] Biological systems such as milk and blood[6] are also affected in similar ways.

In our system, where only metal particles and solvent are present (no ions and no polymers), the question of a stabilization mechanism is quite intriguing and will be discussed.

Results

The following scheme was used to prepare stable Pd–solvent colloidal solutions[13] with acetone as an example:

$$Pd\ atoms + CH_3COCH_3 \xrightarrow[\text{concondense}]{77\ K}$$

$$Pd(CH_3COCH_3)_x \xrightarrow{\text{slow warmup (1.5 h)to room temperature}}$$
$$\text{stage I}$$

$$(Pd)_n(CH_3COCH_3)_y$$
$$\text{stage II}$$

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Table I. Electrophoresis Studies of Pd–Acetone Colloids

solvent	concn, M	velocity of migration, mm/h	particle size (average), nm
acetone	0.0308	3.3	8
acetone	0.0360	3.3	8
acetone	0.0038[a]	8.0	8
acetone	0.0170[a]	8.0	6
acetone	0.0138[b]	8.3	8
acetone	0.0228[a]	6.0	6
acetone	0.0200	c	8
acetone	0.0096[d]	10.0	8
ethanol	0.0416	3.0	8

[a] Au wire connected to left electrode on bottom reactor, also Cu wire connected to ground. [b] A Pd–Au bimetallic colloid. [c] It was impossible to carry out electrophoresis since the colloid mixed with the solvent. In this experiment during the warmup the left electrode was connected to the negative pole of a battery. [d] During the warmup the left electrode was connected to the positive pole of a battery.

The colloidal particles obtained at stage II were air-stable and remained in solution indefinitely. A series of black colloidal solutions using different concentrations and slightly different procedures was prepared (Table I). In order to learn more about these particles several measurements and studies were carried out.

Colloidal Particle Studies. (1) Electrophoresis. Generally, aqueous metallic colloidal particles carry some negative charge,[8] and the rate of migration of these particles to a positive pole can be determined as the electrophoretic mobility (μ_E). For our 0.0308 and 0.0360 M Pd–acetone solutions (8-nm particles) the velocity of migration was reproducibly 3.3 mm/h (see Table I).

$$\text{field strength} = X = E/l = -12.67\ V/23.5\ cm = -0.539\ V/cm$$

$$\text{velocity} = v = 3.3\ mm/3600\ s = 9.17 \times 10^{-4}\ mm/s\ \text{(for 8-nm particles)} = 9.17 \times 10^{-5}\ cm/s$$

$$\mu_E = v/X = (9.17 \times 10^{-5}\ cm/s)/(-0.539\ V/cm) = -17.0 \times 10^{-5}\ cm^2/(V\ s) = -1.7 \times 10^{-8}\ m^2/(V\ s)$$

The above value of μ_E is similar to those reported for a variety of aqueous colloidal particles, e.g., colloidal gold, $30\text{–}40 \times 10^{-5}$ (<100-nm particle diameter); colloidal platinum, 20×10^{-5} (<100 nm); colloidal lead, 12×10^{-5} (<100 nm); and oil droplets, $32 \times 10^{-5}\ cm^2/(V\ s)$ (2000 nm).[14,15] It is interesting to note the similarities of these values regardless of particle size, which suggests that larger particles possess much higher overall charge.

The Debye–Hückel approximation may be used to express the charge density as a function of potential if it is low.[16] The potential at the surface of the particle is defined as the ζ potential. The ζ potential can be calculated according to the convention of Hunter[17] and the Hückel equation:

$$\mu_E = 4\Pi\epsilon_0 D\zeta/6\Pi\eta = 2\epsilon_0 D\zeta/3\eta$$

where for acetone D is the dielectric constant (20.7), ϵ_0 the

(13) Metal atom chemistry and techniques have been described in: Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic: New York, 1980.

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Table II. Pd Films Prepared from Colloid Solutions with Organic Solvents

solvent	concn, M	% Pd	% C	% H[a]	colloid particle size, nm
acetone	0.0236–0.0588[b]	79.70	4.90	0.58	10–14
acetone	0.0588 (500 °C)[c]	88.47	2.30	0.07	
ethanol	0.0178–0.0416	73.43	4.40	0.85	unresolved
acetone	0.0138[d]	25.35 (55.29)[d]	5.45	0.77	8
thf	0.0148	79.70	3.30	0.56	6
2-propanol	0.0108	79.90	6.00	1.10	6

[a] Microanalyses were obtained from Galbraith Laboratories. [b] Average from several colloids within this range of concentrations. [c] Film after heating at 500 °C. The % C varied from 0.4 to 2.5 over several samples. The % H varied from 0.03 to 0.07, while the % Pd varied from 88.3 to 88.5. [d] (Au–Pd)–acetone colloid; % Au in parentheses.

permittivity (8.854×10^{-12} F/m), and η the solvent viscosity (3.16×10^{-4} N-s/m^2).

$$\mu_E = [(\tfrac{2}{3})(8.854 \times 10^{-12})(20.7)\zeta]/[3.16 \times 10^{-4}]$$

$$\zeta = (2.58 \times 10^6)\mu_E$$

$$\zeta = (-1.7 \times 10^{-8})(2.58 \times 10^6)$$

$$\zeta = -4.39 \times 10^{-2} \text{ V} = -44 \text{ mV}$$

The above value for ζ compares well with those reported for a variety of aqueous sols, i.e., 18–58 mV.[14] Such comparisons are tenuous, however, since the equations derived and the data accumulated in the literature are for aqueous systems. Much more work with nonaqueous media is needed.
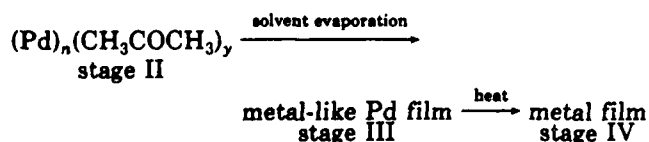
It is interesting to note that when a gold ground wire or a wire connected to either pole of a 12-V battery was immersed in the solution as colloid formation took place, more highly charged particles resulted, and ζ potentials of greater than 100 mV were calculated (Table I compares rates of migration).

(2) Flocculation. Various electrolytes were added to the Pd/acetone colloidal solutions in order to induce flocculation.[8] Three solutions, 0.01 M NaI, CaI$_2$, and AlBr$_3$, were prepared in acetone, respectively. Addition of NaI solution to a 0.0175 M Pd/acetone colloid in a Na:Pd ratio of 1:1 caused flocculation to begin in 5 min at room temperature. Addition of CaI$_2$ solution to the same colloid in the same ratio caused flocculation to begin in 3 min. Finally, addition of AlBr$_3$ solution to the colloid in the same M:Pd ratio induced flocculation in 2 min. These results are in agreement with data reported by Furlong[7] in which high-valent cations induced flocculation faster than monovalent cations. Addition of water to the colloid induced flocculation only after 120 h at room temperature.

(3) pH Measurements. No evidence for increased acidity or basicity was obtained by measuring the pH of the colloidal solutions. The same values for pure acetone were observed (pH 7.7).

(4) Other Solvents. Ethanol, isopropyl alcohol, and acetone–isopropyl alcohol mixtures all worked very well as solvents for Pd colloidal formation and stabilization. Ethanol allowed slow flocculation after about 24 h, although with the other solvents indefinite colloid stability was observed (room temperature).

Thin Films. Stage II can be converted to stages III and IV:

$$(Pd)_n(CH_3COCH_3)_y \xrightarrow{\text{solvent evaporation}}$$
stage II

$$\text{metal-like Pd film} \xrightarrow{\text{heat}} \text{metal film}$$
stage III   stage IV

Stage III was prepared by slowly dripping the colloidal solution onto a substrate. Solvent evaporation was speeded by applying a vacuum or N$_2$ gas flow or by using a warm substrate. Stage III was also prepared in uniform thin

Table III. Products Evolved upon Heating Films Derived from Pd–Acetone Colloidal Solutions

temp, °C	products (relative %)
100	H$_2$O (25.6), CO (41.2), CO$_2$ (11.8), (CH$_3$)$_2$C=O (13.2)
200	H$_2$O (8.4), CO (27.7), CO$_2$ (2.3), CH$_3$CH=CHCH$_3$ (24.7), (CH$_3$)$_2$C=O (36.5)
350	H$_2$O (5.9), CO (21.2), CO$_2$ (3.1), C$_3$H$_6$ (2.7), C$_4$H$_2$ (0.3), C$_4$H$_4$ (0.2), C$_2$H$_5$OH (0.7), CH$_3$CH=CHCH$_3$ (28.8), (CH$_3$)$_2$C=O (37.5)

[a] The film was obtained by stripping the acetone solvent under vacuum at room temperature for 3 h. Initial concentration of the colloid was 0.0521 M.
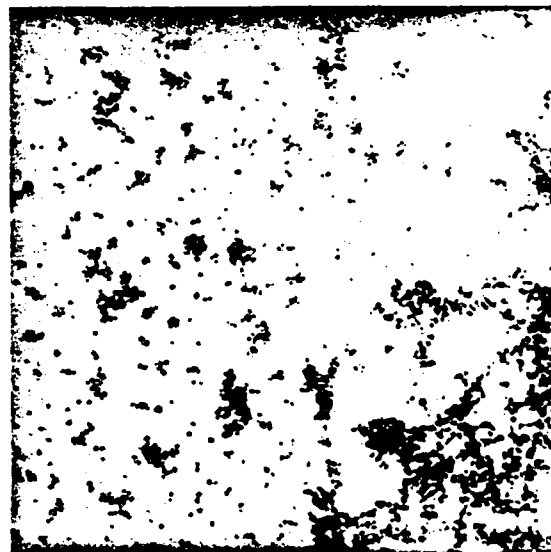

Figure 1. Transmission electron micrograph of particles derived from a Pd–acetone colloid (very dilute solution; 2.5×10^5 magnification). (About 8-nm particles.)

films by spraying the solution as an aerosol. Stage IV was obtained by heating stage III under vacuum or in a stream of N$_2$. Films from stages III and IV were analyzed and characterized in a variety of ways as follows.

Thin-Film Analysis. (1) Elemental Analyses and Pyrolyses. Stage III, after drying at 10^{-3} Torr for 3 h, still contained substantial portions of carbon and hydrogen (Table II). Vacuum pyrolysis at 500 °C to reach stage IV caused the evolution of mainly acetone along with some carbon dioxide.

A more detailed pyrolysis study using GC–MS was carried out at temperatures of 25, 100, 200, and 350 °C. Table III indicates the products that were successively evolved. At the lower temperatures acetone was the main product while at higher temperatures butenes, propene, and other similar products were evolved.

(2) IR Studies. Infrared analysis of the stage III film indicated the presence of only adsorbed acetone. Strongest absorption was at 2980 and 1740 cm^{-1}, similar to pure acetone.

Figure 2. Scanning electron micrograph of film (stage III) derived from a Pd–acetone colloid (1.1×10^5 magnification).

Table IV. Resistivities of Films (Stages III and IV) Derived from Pd–Acetone Colloids

solution concn, M	resistance, Ω/cm^2	thickness, μ	resistivity ρ ($\times 10^2$), Ω cm
0.0165	71–93[a]	40–60	3.5–4.6
0.0165[b]	43	40	2.2
0.0298	82–107	65	53–69
0.0228	49–109	4.0	1.9–4.4
0.0138[c]	380	1.6	6.1
Pd film[d]	357	0.28	0.10
Pd bulk[e]			11×10^{-4}
cis-[CH(AsF$_5$)$_{0.14}$][f]	h		0.18
TTF·TCNQ[g]	h		0.14

[a] Values varied within this range by measuring resistivities of different sections of the film. [b] The film was heated for 1 h at 200 °C, and then resistance was measured. [c] A Pd–Au bimetallic colloid solution. [d] A pure Pd film for comparison (prepared by vacuum deposition of Pd vapor). [e] *Handbook of Chemistry*, 57th ed.; CRC: Boca Raton, FL, Vol. 20, p E84. [f] Polyacetylene, doped with AsF$_5$. [g] Measured on a single crystal in the direction of greatest conductivity. [h] Not reported.

(3) SEM and TEM Studies. Dilute solutions were dripped onto carbon-coated copper grids so that acetone evaporation left isolated particles. According to transmission electron microscopy (TEM) the particles were spherical and had a tendency to link together (Figures 1 and 2).

Scanning electron microscopy (SEM) showed that the film formed by acetone evaporation was made up of a series of strands or chains of colloidal Pd particles that were intertwined. When the film was heated, these strands collapsed to a more uniform film (Figure 3).

(4) Resistivity. Films of different thickness (2.8–65 μm) were prepared by dripping the colloidal solutions onto a glass plate. The values of thickness and resistance are summarized in Table IV. After the films were heated, resistivity decreased.

(5) Reaction with $(C_6H_5)_2P(C_2H_5)$. After solvent evaporation at room temperature the resultant Pd film (25 mg) was treated with excess $(C_6H_5)_2P(C_2H_5)$ under nitrogen. After the mixture stirred for 48 h under nitrogen the volatiles were removed, separated, and identified. Besides excess phosphine, only acetone (0.39 mg or 6.8×10^{-3} mmol) was collected. This corresponds to about 1.6% of the total weight of the sample.

Discussion

The novel features regarding these materials are that the particles are stable toward flocculation in nonaqueous
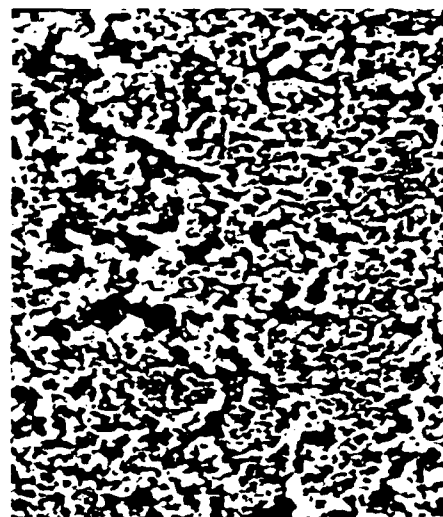

Figure 3. Scanning electron micrographs of films (stage IV) derived from a Pd–acetone colloid: (top) after heating at 180 °C (3×10^4 magnification); (bottom) after heating at 500 °C (1×10^4 magnification).

solvents and they are living colloids in that the particles grow to films under very mild, controlled conditions. We will now consider what is known about formation and stabilization mechanisms for these materials.

The growth of colloidal particles from solvated atoms is in competition with the reaction of the atoms and growing particles with solvent medium.[18] As would be expected, one process being favored over the other depends on what metal and what solvent are interacting. In the case of nonpolar solvents and reactive metals, such as Fe, Co, or Ni, extensive bond-breaking reactions have been observed (e.g., Ni with pentane).[19] However, more polar solvents with better ligating properties tend to solvate the metal species with less bond breaking of the solvent molecules. In other words, solvent *molecules* complex with the metal species rather than *fragments* of the solvent.

In the case of Pd–acetone colloidal particles, we have found no evidence for adsorbed species other than acetone itself. Thus, vacuum treatment of stage III at room temperature and 100 °C yielded only acetone as a volatile

(18) Klabunde, K. J.; Tanka, Y. *J. Molec. Catal.* **1983**, *21*, 57–79.
(19) Davis, S. C.; Severson, S.; Klabunde, K. J. *J. Am. Chem. Soc.* **1981**, *103*, 3024–3029.

product. At higher temperatures products were evolved that were probably formed from catalytic/pyrolytic decomposition of acetone. In addition, ligand displacement by excess $(C_6H_5)_2P(C_2H_5)$ yielded only acetone, and IR studies suggest that the only displaceable organic material is acetone itself. But note that it is quite strongly coordinated, requiring a vacuum and warming for just partial removal. A strong solvation mode is apparently important. On the metal cluster surface a variety of binding schemes may be operational, as suggested by Weinberg and Templeton[20] for acetone on a Ru(001) surface:
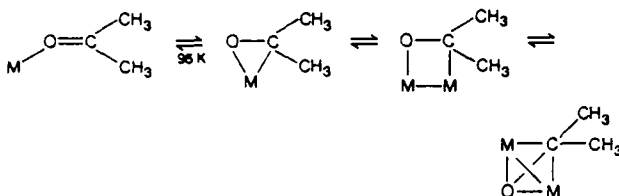
As our Pd particles grow to hundreds of atoms, solvent molecules would be incorporated within the particles and on the outside. As growth continues, some solvent molecules must be displaced by incoming atoms and smaller metal particles. Eventually the particle growth stops. At what point it stops (ultimate particle size) depends on the initial metal concentration in the matrix and the matrix warmup procedure.

Metal Concentration. Initial metal concentration can affect colloid particle size in a kinetic way, since it is unlikely particle growth is reversible under such conditions.[21] Once a Pd–Pd bond is formed, it does not break. Therefore, in a dilute solution of atoms, the frequency of encounters will be lower. As the metal atom–solvent matrix warms and the atoms and the forming particle become mobile, it is the number of encounters that occur during the period before particle stabilization that is important. And if metal concentration becomes too high, particle size becomes too large, causing precipitation. Similar behavior has been encountered for gold colloids in acetone.[21] Interestingly, however, gold particle size could be more easily controlled by concentration effects.[21] With palladium we invariably obtained particle sizes of 6–12 nm. Low concentrations of Pd still yielded 6–8-nm particles, and high concentrations of Pd yielded 8–12-nm particles plus much larger particles that precipitated. Thus, there is a distinct preference for an 8-nm average particle size for Pd in acetone as well as for Pd in ethanol. We do not fully understand this selectivity yet, although particle stabilization must be the key, as discussed below.

Particle Stabilization. We believe particle growth stops because of two factors. The first comes under the heading of steric stabilization.[6] Solvent molecules must be displaced and reordered on the surface of a Pd cluster if another cluster is to chemically bind to it. As the particles (clusters) become more massive the kinetic energy goes down, and perhaps the energy requirement for solvent displacement/reordering becomes large compared to the kinetic energy of the sluggish larger particles.

A second mode of stabilization is electronic in nature. Electrophoresis experiments clearly show that the Pd particles bear negative charge. Although it is difficult to determine accurately the number of negative charges each particle possesses (formulas derived for such calculations are based on aqueous systems), it is clear that these negatively charged particles will repel each other and therefore aid their stabilization. ζ potentials are indicative of substantial electronic stabilization.

How is this negative charge acquired? One possibility is that free radicals are involved, perhaps formed by pyrolytic decomposition of small amounts of acetone on the hot metal vaporization source or by reactions of acetone with metal atoms. A number of radiolysis studies of metal colloids in water–acetone solutions indicate that organic radicals do transfer electrons to the particles which act as electron reservoirs (and can behave as catalysts for water reduction).[22,23]

$$(CH_3)_2\dot{C}OH + (Ag)_m \rightarrow (CH_3)_2C^+\text{-OH} + (Ag)_m^- \rightarrow$$
$$CH_3COCH_3 + H^+ + (Ag)_m^-$$
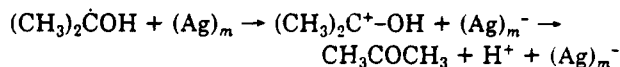
If free radicals were involved in our system, the generation of H^+ in solution would be expected. However, we have found no evidence of H^+ in our solutions nor have we found any radical recombination products that might be expected. Therefore, we do not believe free radicals are important in the generation of negatively charged metal particles in our system.

A second possibility is that the electron affinity of the particles may allow them to acquire electrons from the reaction vessel walls, electrodes, and solvent medium. Such a process would help explain the need for a slow warmup procedure in order to yield stable colloidal solutions since scavenging of electrons may be a slow process.

Actually, this type of electrostatic charging of colloidal particles is not uncommon. Oil droplets, for example, scavange electrons from aqueous solution.[14]

If scavenging occurs during the warmup period, we reasoned that by inserting a gold ground wire into the solution during colloid formation some change would be realized. Indeed, with this procedure the resulting Pd particles became more highly negatively charged according to electrophoresis studies (Table I). The next step was to place a wire attached to the negative pole of a 12-V battery into the solution during colloid formation. In this case electrophoretic behavior changed markedly, and measurements were impossible due to uncontrolled mixing. A last case was to attach the wire to the positive pole of the battery, and this again caused a significant change in the behavior of the colloid. The migration rate was the highest measured (Table I), and the colloid was very stable. Since a circuit was not complete, either pole of the battery simply served as a reservoir of electrons, and more electrons were available, yielding more negatively charged particles.

On the basis of the above observations, we believe particle stabilization occurs slowly during the warmup period by steric effects (solvation) and by electronic effects, where the growing particles develop and possess a sufficiently high electron affinity that electron scavenging from the reactor environment is possible. This scavenging can be affected by the presence of electron sources, and electrophoretic mobilities increased. Such experimental manipulations hold promise for controlling electrophoretic mobilities and perhaps particle size.

Further support for this electronic stabilization mechanism is found in our studies of electrolyte additions. It is known that electrolytes added to aqueous metal colloids aid the breakdown of the charged double layer, which in turn allows particle flocculation.[8,14,15] Our studies with electrolytes yielded similar results. The electrolytes with

(20) Templeton, M. K.; Weinberg, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 774-779.

(21) Franklin, M. F.; Klabunde, K. J. *High Energy Processes in Organometallic Chemistry*; Suslick, K. S., Ed.; ACS Symposium Series 333; American Chemical Society: Washington, DC, 1987; pp 246-259.

(22) Henglein, A. *J. Am. Chem. Soc.* **1979**, *83*, 2209-2216.

(23) Henglein, A.; Lillie, J. *J. Am. Chem. Soc.* **1981**, *103*, 1059-1066.

the more highly charged cations caused flocculation more quickly (Al^{3+} > Ca^{2+} > Na^+). This is a classic case showing not only the existence of charged colloidal particles but also that a charged double layer must exist.[14]

Living Colloids → Films. From Table II it is evident that substantial portions of organic residue remain in the films after solvent stripping at room temperature. We found that the films were susceptible to oxidation, as might be expected, and oxygen (by difference) ranged as high as 25%. If care was taken to prevent oxidation, an empirical formula of about $Pd_5C_2H_2O_2$ was determined. An average of all determinations indicated $Pd_9C_5H_7O_{11}$. After treatment at 500 °C, causing the evolution of some organic material, an average empirical formula of $Pd_4C_1O_3$ was determined.

Earlier discussion suggested that while in solution the colloidal particles are solvated by acetone, and other organic fragments were not detected. However, upon solvent stripping it is obvious from the empirical formulas that acetone must be breaking up, accompanied by some oxidation. Some acetone is still present since it is the main volatile product evolved at 300 °C (Table III) and the only volatile product displaced by $(C_6H_5)_2P(C_2H_5)$. Since the remaining fragments must be very rich in carbon and oxygen, the formation of palladium carbides and palladium oxides is likely.

Electron microscopy studies show that the individual colloidal particles are spherical and have a tendency to link together in chains. The initial film appears to be made up of a network of Pd particle chains (Figure 2). Heating the film causes these chains to collapse to a more uniform film (Figure 3).

Resistivities of these films are of interest. Table IV lists values determined for 1 cm^2 films of varying thickness (0.2–60 μm). The initial films are conductive and increase in conductivity after heating. They behave more like semiconductors than pure metals, and actually their resistivities are similar to those of doped organic polymers.[24]

Conclusions

Palladium atoms dispersed in excess acetone (or other solvents) begin to cluster upon warming. The properties of the resultant colloidal particles depend slightly on initial metal concentrations, warmup procedures, and the availability of electrons. During colloid formation the particles are stabilized by solvation effects and by electronic effects due to electron scavenging (the Pd particles behave as electron sinks). Upon solvent removal, films of intertwined chains of spherical Pd colloidal particles (still containing organic residues) are formed. Heating the film causes these chains to collapse to a uniform film with a decrease in resistivity. Some organic residue remains in the films.

Experimental Section

Preparation of a Typical Pd–Acetone Colloid. The metal atom reactor has been described previously.[13,25] As a typical example, a W–Al$_2$O$_3$ crucible was charged with 0.80 g of Pd metal (one piece). Acetone (300 mL, dried over K$_2$CO$_3$) was placed in a ligand inlet tube and freeze–pump–thaw-degassed with several cycles. The reactor was pumped down to 1 × 10^{-4} Torr while the crucible was warmed to red heat. A liquid N$_2$ filled Dewar was placed around the vessel, and Pd (0.5 g) and acetone (189 g) were codeposited over a 1.0-h period. The matrix was dark-brown at the end of the deposition. The matrix was allowed to warm slowly

under vacuum by removal of the liquid N$_2$ filled Dewar for 1.5 h.

Upon meltdown a black solution was obtained. After addition of nitrogen the solution was allowed to warm for another 0.5 h to room temperature. The solution was siphoned out under N$_2$ into Schlenk ware. Based on Pd evaporated and acetone inlet the solution molarity could be calculated.

Effects of a Ground Wire and a Battery-Attached Wire. Several experiments were carried out where a gold wire was connected to an electrode inside the reactor so that it reached the bottom of the reactor. A copper wire was attached to the upper part of the electrode external to the vacuum chamber. This wire was either grounded or attached to the negative or positive pole of the 12-V storage battery. Colloidal solutions obtained by using these modifications did not show any marked changes in stability, but electrophoretic mobilities increased.

Electrophoresis Experiments. The electrophoresis experiments were carried out by using a glass U-tube of 11.0 cm with a stopcock on the base to connect a perpendicular glass tube (13 cm long × 35 cm high).[14,26] Platinum electrodes were attached to the top of the U-tube and through a ground glass joint to the pole of a 12-V battery. The acetone was placed in the U-tube, and then the colloid solution was added slowly through the side tube. The migration rate was determined on the basis of the average of the displacement in each side of the U-tube. A typical experiment was carried out for a period of 3 h at 25 °C.

Electrolyte Additions. A study of flocculation times was carried out by using a 0.010 M NaI solution. In a test tube 2 mL of colloidal solution (0.0175 M) and 2 mL of NaI were added at room temperature (25 °C). After 5 min flocculation of the colloid was observed.

A solution of 0.010 M CaI$_2$ in acetone was also prepared. By use of the same ratio as before, flocculation of the colloid began after 3 min. Finally, a 0.010 M AlBr$_3$ acetone was prepared. Addition to the colloid in the same amount as before induced flocculation after 1 min at room temperature. Complete flocculation was observed after 10, 8, and 7 min, respectively.

In other experiments water was added to the colloid solution, and after 120 h flocculation was observed.

GC–MS Experiments. GC–MS pyrolysis was carried out by using a Porapak Q 6-ft column (flow rate 35 mL/min) attached to a Finnigin 4000 quadrupole GC–MS. The sample was placed in a stainless steel tube 10 cm long connected to a four-way valve. One of the outlets was attached to a Porapak Q column interfaced with the M.S. The stainless steel tube containing a portion of Pd colloid film (stage III) was placed in a furnace connected to a Variac provided with a digital quartz pyrometer to measure the temperature. Three pyrolyses were performed at 100, 200, and 350 °C with the Pd–acetone film (from colloid, 0.0521 M).

Addition of $(C_6H_5)_2P(C_2H_5)$. A Pd film was prepared by evaporating the solvent from a 0.035 M colloid solution. A 25-mg sample of the film was treated with 1.5 mL of $(C_6H_5)_2P(C_2H_5)$ (5.6 mmol) under a nitrogen atmosphere. After 48 h at room temperature with stirring, the dark solution became lighter. The volatiles were pumped out through 263 and 77 K traps. The 77 K trap contained only acetone (0.39 mg or 6.8 × 10^{-3} mmol), identified by gas-phase IR.

SEM and TEM Studies. Electron micrographs were obtained on a Jeol, Temscan-100 CX11 combined electron microscope and a Hitachi HV-11B (TEM) operated at 2 × 10^5 magnification. The specimens for TEM were obtained by placing a drop of the colloid solution on a copper grid coated by a carbon film. The samples for SEM were placed between two copper grids one of which was coated by a carbon film.

Resistivity Studies. Films of different thickness (02.8–65 μm) were prepared by dripping the colloidal solutions onto a glass plate edged with silicon rubber adhesive resin. The acetone was allowed to evaporate. Resistivities were measured by scraping the silicon rubber away from the edges of the film, which was then trimmed to rectangular shape. It was then connected to electrodes on each end by vapor deposition of an opaque film of aluminum or copper. To get a reliable contact on aluminum, it was necessary to apply a spot of silver paint over the aluminum. This was not necessary

(24) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361–381.
(25) Klabunde, K. J.; Timms, P. L.; Ittel, S.; Skell, P. S. *Inorg. Synth.* **1979**, *19*, 59–86.

(26) Shaw, D. J. *Electrophoresis*; Academic: New York, 1969.

with copper electrodes. The resistance of each sample was measured with a Keitley 178 Model digital multimeter. the vapor depositions were carried out with a Veeco Model VS-90 metal evaporator. the values of thickness and resistance are summarized in Table IV.

Solubility Studies. The solubility of the Pd–acetone film (0.0236 M) was tested with the following solvents: acetone, ethanol, THF, DMSO, benzene, toluene, and pentane. The films were completely insoluble after 24 h of contact with stirring at 25 °C.

Infrared Studies. Infrared spectra were recorded on a Perkin-Elmer PE-1330 infrared spectrometer. IR studies of the metal films using either KBr pellets or Fluorolube yielded only evidence for ν_{C-H} (2980 cm^{-1}) and ν_{CO} (1740 cm^{-1}) showing the same shape as the acetone standard.